

VI.4 A Thin Film, Anode-Supported Solid Oxide Fuel Cell based on High Temperature Proton Conducting Membrane for Operation at 400 to 700°C

Objectives

- Measure conductivity of K-doped and Y-doped BaZrO₃ (KBYZ) in H₂-H₂O and air-H₂O containing atmospheres over a range of temperatures from 400 to 700°C.
- Fabricate KBYZ thin film, Ni + KBYZ anode-supported button cells (at least 2 cm² active area) with a two phase, composite mixed ionic electronic conducting (MIEC) perovskite cathode, comprising a proton conductor (KBYZ) and an electronic conductor.
- Conduct electrochemical tests on button cells with humidified H₂ as fuel and air as oxidant over a range of temperatures from 400 to 700°C.

Accomplishments

- The chemical stability of BaZrO₃ over BaCeO₃ was confirmed from thermodynamic calculation.
- The procedure for powder preparation using planetary milling was established.
- Experimental test and analysis systems were set up.

Introduction

The key attribute of an oxygen ion-conducting electrolyte for the solid oxide fuel cell (SOFC) has one significant and unavoidable shortcoming, namely fuel dilution. Since water vapor (and CO₂ if CO is in the fuel) are formed at the anode, the fuel continually becomes depleted, which is undesirable. Fuel dilution can be avoided provided a proton conducting solid electrolyte is used, since in such a case the water vapor

is produced at the cathode where it mixes with excess air and does not significantly lower the cell voltage. Since fuel dilution can be avoided, at all times during cell operation, the pressure of hydrogen can be maintained at a value near the feed composition, which leads to little anode concentration polarization and relatively low anode activation polarization due to high hydrogen partial pressure. These advantages are expected to facilitate more efficient operation of the SOFC based on proton conducting membranes. A fuel cell based on high temperature proton conductor (HTPC) has other important attributes such as thermal integration capabilities and no CO poisoning which allows the use of non-precious metal catalysts.

High temperature proton conductors are based on perovskite type materials (ABO₃) containing oxygen vacancies. Such materials can absorb water vapor and become proton conductors. Of the materials investigated to date, doped BaCeO₃ exhibits the highest proton conductivity. Thus, much work has been conducted on this material and another ceria-based material, SrCeO₃ which also exhibits high proton conductivity. The very low stability of these cerates, however, has been a problem [1]. It was experimentally shown that BaCeO₃ decomposes in the presence of liquid water [2]. Studies have also shown that BaCeO₃ and SrCeO₃ are not stable in CO₂-containing atmospheres below 800°C [3,4]. Even though fuel cells made using these materials may not present a significant problem for limited periods of time at higher temperatures, their long term stability is problematic on repeated thermal cycling and especially when used in a thin film form as required for an SOFC. Other materials of interest from the standpoint of conductivity are rare earth oxide doped BaZrO₃ and Ba₃Ca_{1-x}Nb_{2-x}O_{9-δ} (BCN), although these materials exhibit lower conductivity than BaCeO₃ and SrCeO₃.

Approach

In addition to the ability to dissolve water vapor into the lattice and transport protons, the stability of the material in water vapor must be demonstrated. Work done to date has demonstrated that unlike BaCeO₃ and SrCeO₃, materials such as BaZrO₃ or BCN are stable in water. Their stability has been demonstrated by heat-treating them in an autoclave at temperatures as high as 500°C and water vapor pressures as high as 180 bars [5]. Somewhat lower proton conductivity of BaZrO₃-based HTPC compared to BaCeO₃ and SrCeO₃ is related in part to the lower overall basicity. For proton conduction, it is necessary that a sufficient

Joon-Ho Koh (Primary Contact), Mick Barton
Materials & Systems Research, Inc.
5395 West 700 South
Salt Lake City, UT 84104
Phone: (801) 530-4987; Fax: (801) 530-4820
E-mail: jkohl@msrihome.com

DOE Project Manager: Lane Wilson
Phone: (304) 285-1336
E-mail: Lane.Wilson@netl.doe.gov

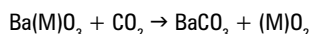
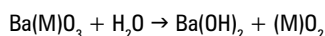
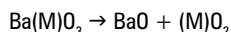
Subcontractor: Dr. Anil V. Virkar
The University of Utah, Salt Lake City, UT

amount of H_2O dissolve into the perovskite lattice. The affinity towards water vapor can be described in terms of basicity of the material. It is known that for the A-site of perovskite materials (ABO_3), basicity increases in the order $\text{Sr} \rightarrow \text{Ba}$, and for the B-site it increases in the order $\text{Zr} \rightarrow \text{Ce}$. The lower proton conductivity of BaZrO_3 thus in part is attributed to its lower basicity.

The suggested approach is to start with a material of proven stability, such as BaZrO_3 , but then add other elements (dopants) to enhance its basicity. The most basic ions are the alkali ions such as sodium and potassium. At 1,000 K, the partial pressure of H_2O for the formation of $\text{Ba}(\text{OH})_2$ is ~ 0.45 atm, while that for the formation of KOH (alkali earth metal hydroxide) is only $\sim 3 \times 10^{-7}$ atm. Thus, the incorporation of potassium into the perovskite lattice should significantly increase affinity for H_2O , and thus should enhance protonic conductivity. Doping on the B-site with an alkali ion, however, will not be feasible due to the large difference in electrical charge (+1 vs. +4) and also due to the larger size of alkali ions, with the exception of lithium, compared to the typical B-site ion. However, the ionic sizes of divalent alkaline earth ions (Ba, Sr, etc.) are comparable to monovalent alkali ions (Na, K, etc.). Thus, the suggested approach is to dope on the A-site with an alkali ion instead of the usual B-site to create oxygen vacancies. In addition, a small amount of yttrium is doped on the B-site for the purpose of preventing possible microcracking associated with tetragonal to monoclinic phase transformation if a small amount of ZrO_2 precipitates form. The resultant material ($\text{K}_x\text{Ba}_{1-x}\text{Y}_y\text{Zr}_{1-y}\text{O}_{3-\delta}$) should have higher affinity towards water uptake (due to the presence of potassium in the lattice), but at the same time, the material should be stable by virtue of the presence of BaZrO_3 as the major constituent.

Results

From a chemical equilibrium point of view, the stability of BaCeO_3 and BaZrO_3 under typical SOFC conditions can be compared by calculation of the free energy changes for the following reactions with (M) = Ce or Zr. Thermodynamic data were obtained from the literature [6,7].



The calculation of the standard free energy changes for these reactions shows that in all cases the reactions of BaZrO_3 require larger values of ΔG° than BaCeO_3 (Figure 1). Therefore BaZrO_3 is less likely to react under the SOFC conditions than BaCeO_3 .

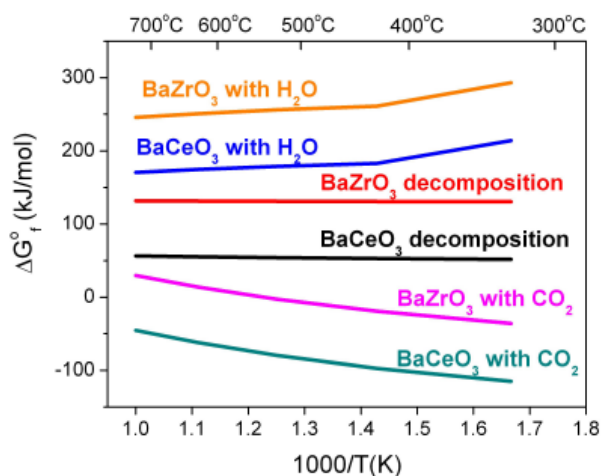


FIGURE 1. Comparison of the Standard Free Energy Changes of BaCeO_3 and BaZrO_3 for Several Reactions: Decomposition, Hydrolysis, and Reaction with CO_2 [Thermodynamic data from Reference (6) for BaCeO_3 and Reference (7) for other compounds]

Powders and samples are currently being processed for experimental tests. Powders of K_2CO_3 , BaCO_3 , Y_2O_3 , and ZrO_2 are mixed in the requisite ratio, and ball-milled. The target K-contents are 10% ($\text{K}_{0.1}\text{Ba}_{0.9}\text{Y}_{0.04}\text{Zr}_{0.96}\text{O}_{3-\delta}$) and 20% ($\text{K}_{0.2}\text{Ba}_{0.8}\text{Y}_{0.04}\text{Zr}_{0.96}\text{O}_{3-\delta}$). The powder mixture is calcined at 1,250°C for 2 hours in a covered zirconia crucible. The calcined powder (which forms doped- BaZrO_3) is ground to nano-size by planetary milling. The planetary mill equipment (Retsch PM-100) has been set up and ready for use (Figure 2).

The past preliminary test did not produce nano-size powders, and the reasons were identified: (a) too much solvent, (b) single-step milling process, and (c) inappropriate size of milling media. The conditions will be improved by adjusting and optimizing media sizes, a ratio of solvent/powder/media, milling time, and rotation speed. A multi-step processing with different media (from large to small) will be employed.

Anode-supported fuel cells will be fabricated by sintering thin KBYZ film on a porous structure of Ni and KBYZ. In order to lower the sintering temperature and minimize the loss of volatile potassium compounds, an average powder size of 250 nm is required. The target sintering temperature is 1,450°C. A porous structure of an electronic conductor and KBYZ as cathode will be printed. The fabricated cell will be tested at 400–700°C for current-voltage characteristics. The test system was prepared and set up as shown in Figure 3. Current interruption tests and measurement of complex impedance spectra will be carried out to evaluate the ohmic resistance and the various polarization contributions. The system for these analyses was set up using an oscilloscope (Agilent 54622A), an

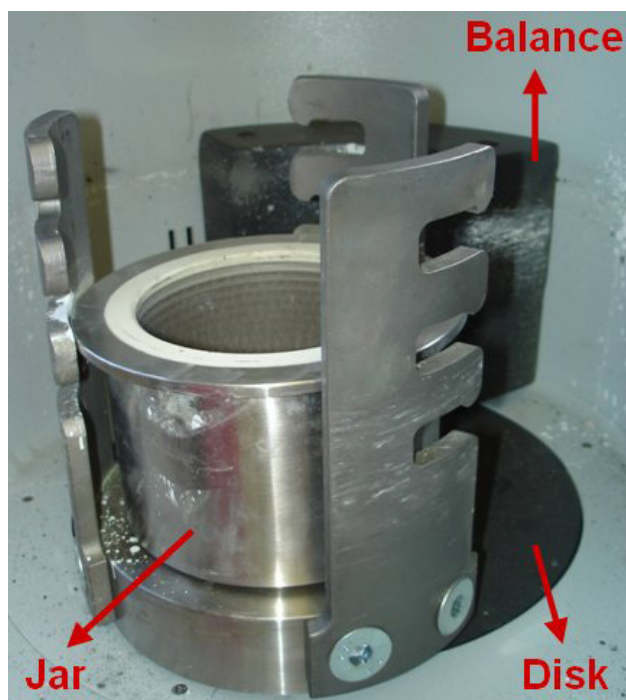


FIGURE 2. A Photo of the Planetary Milling System

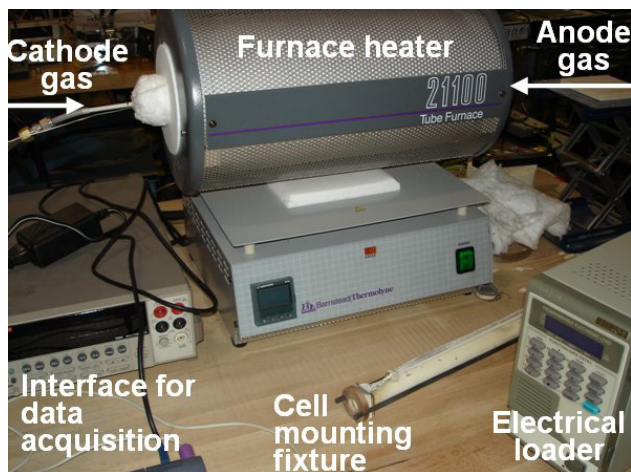


FIGURE 3. A Photo of the Cell Test System

electrochemical interface (Solatron SI 1287), and an impedance analyzer (Solatron SI 1260), as shown in Figure 4.

Conclusions and Future Directions

One of the challenges is to prepare nano-size KBYZ powders that can keep the sintering temperature at or below 1,450°C. The current primary approach is to

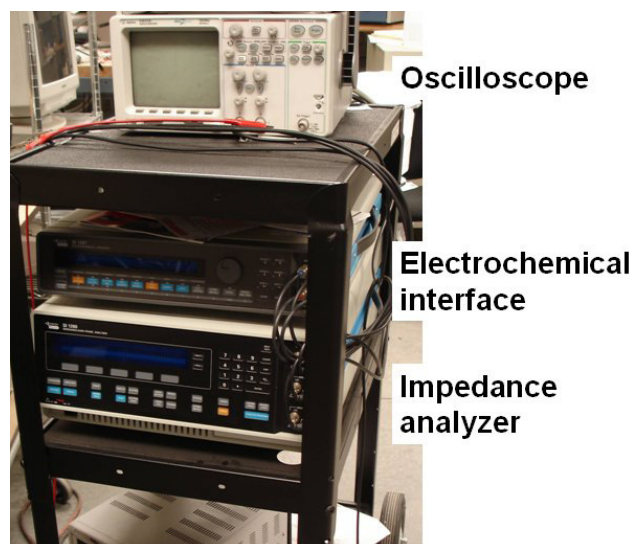


FIGURE 4. A Photo of the Electrochemical Analysis System

use the planetary mill. Alternative approaches based on chemical methods such as combustion synthesis or sol-gel processing will also be considered in the future if necessary.

References

1. "Proton-Conducting Oxides," Kreuer K.D. *Annual Review of Materials Research*. 33 (2003) 333-359.
2. "Stability of BaCeO₃-Based Proton Conductors in Water-Containing Atmospheres," Bhide S.V., Virkar A.V. *Journal of The Electrochemical Society*. 146(6) (1999) 2038-2044.
3. "Synthesis of strontium and barium cerate and their reactions with carbon dioxide," Scholten M.J., Schoonman J., Miltenburg J.C., Oonk H.A.J. *Solid State Ionics*. 61 (1993) 83-91.
4. "Perovskite solid electrolytes: Structure, transport properties and fuel cell applications," Bonanos N., Knight K.S., Ellis B. *Solid State Ionics*. 79 (1995) 161-170.
5. "Transport Properties of Potassium-Doped BaZrO₃ in Oxygen- and Water-Vapor-Containing Atmospheres," Patnaik A.S., Virkar A.V., *Journal of The Electrochemical Society*. 153(7) (2006) A1397-A1405.
6. "The Thermodynamic Properties of BaCeO₃ at Temperatures from 5 to 940 K," Scholten M.J., Schoonman J., Miltenburg J.C.V., Cordfunke E.H.P. *Thermochimica Acta*. 268 (1995) 161-168.
7. "Thermochemical Data of Pure Substances: Parts I and II," (3rd Edition) Barin I. VCH Publication, Weinheim (1995).